

Basic concepts of thermochemistry

Thermochemistry - section of physical chemistry studying thermal effects, accompanying chemical and physical-chemical processes:

- chemical reactions,
- phase transitions,
- formation and dilution of solutions,
- dissociation of molecules of simple gaseous substances into individual atoms,
- dissociation of ion crystals on gaseous ions,
- ionization of atoms as a result or joining electrons).

Basic concepts of
thermochemistry

**Chemical reaction as
thermodynamic process,**

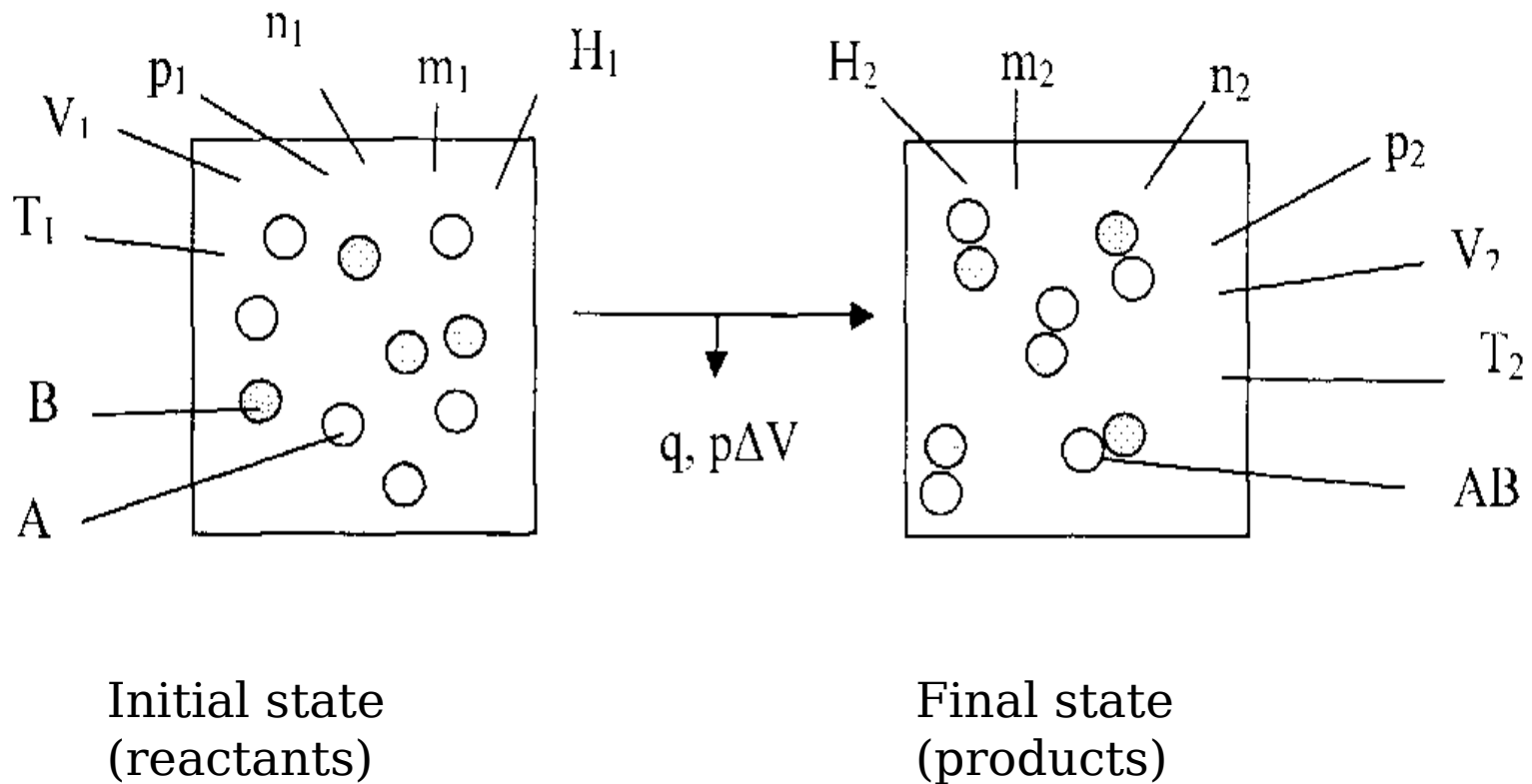
is to turn some substances into
others, by changing the
composition and/or structure.

Let the system react



Basic concepts of thermochemistry

In this case the chemical reaction as a thermodynamic process can be presented as follows:



Basic concepts of thermochemistry

- Chemical reactions can be both **exothermal** if the system releases heat into the external environment as well as **endothermic**, if the system absorbs heat from the environment.

Exothermic vs Endothermic Reaction

- **Exothermic Reaction**

- Heat flows out of the system to the surroundings
- Amount lost by system exactly the same as amount gained by surroundings *

- **Endothermic Reaction**

- Heat flows is into a system from the surroundings.
- Amount gained by system is exactly the same as amount lost by surroundings*

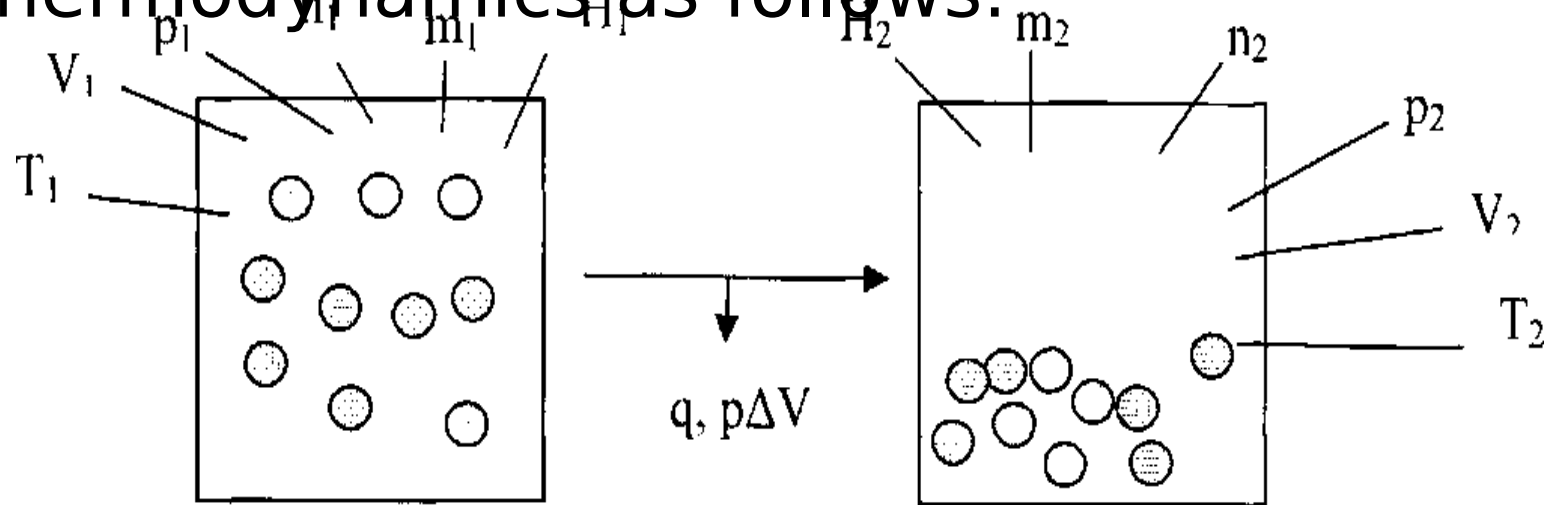
Phase transition

- The transition of the substance from one phase to another, associated with qualitative changes in the properties of the substance.
- Examples of phase transitions are changes in the aggregate state of the substance, the transition of crystalline substance from one modification to another.
Phase transitions can also be both exothermic and endothermic.

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Phase transition

Let substance A pass from a gaseous state to a liquid state, the phase transition can be presented from the point of view of thermodynamics as follows:



Initial state (Substances
A in gas faze)

Final state
(Substances A in
liquid state)

The thermal effect of these processes allows us to determine the most important physical values that characterize the properties of the substance:

- ***bond energy (molecule strength measure),***
- ***energy of ionization and affinity for electron (a measure of oxidative and restorative ability of simple substances),***
- ***energy of the crystal lattice (a measure of crystal lattice strength).***

Thermochemical equation - conditional image of the physical and chemical process, in which in addition to formulas and aggregate states of the substance, indicates the thermal effect:

- *chemical reaction: $A(g) + B(s) \longrightarrow C(l) - Q$*
or
- $A(g) + B(s) \longrightarrow C(l) - \Delta H$
- *phase transition: $A(g) \longrightarrow A(l) + Q$ or*
- $A(g) \longrightarrow A(l); -\Delta H$
- *dissolving the substance:*
- $A(\text{solid}) \longrightarrow A(\text{solution}) + Q$ or
- $A(\text{solid}) \longrightarrow A(\text{solution}) ; -\Delta H$

Heat effect

- **Heat effect** (Q , kJ/mole) - energy that is released or absorbed in the form of heat, with the irreversible flow of the physical and chemical process provided:
- T , p const or T , v const, the system makes only the work of expansion ($A=0$).
- If the process is carried out in the autoclave: $V = \text{const}$ thermal effect is equal to internal energy
 - $Q_v = - \Delta U$.
- *If the process is carried out in an open system (which is most common) when $p = \text{const}$ thermal effect is equal to enthalpy:*
 - $Q_p = - \Delta H$.

Standard heat effect

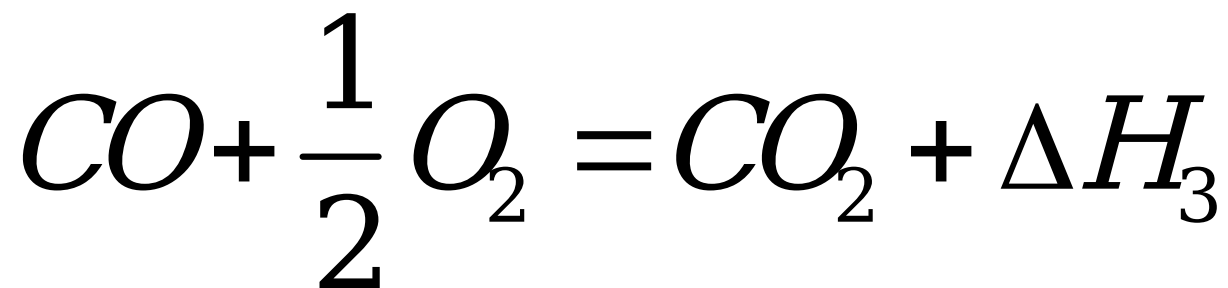
- **Standard heat effect** is the heat of the physical and chemical process, which occurs under standard conditions: $T = 298\text{K}$, $p = 101.3\text{ kPa}$.
- At the same time, solid and liquid substances are in a stable modification, gases are close to the state of ideal gas.
- The standard thermal effects are experimentally identified and presented in special reference books.
- There are several ways of expressing the thermal effects of physical and chemical processes

Conventional Definitions of Standard States

- For a Compound
 - For a gas, pressure is exactly 1 atm.
 - For a solution, concentration is exactly 1 M .
 - Pure substance (liquid or solid)
- For an Element
 - The form $[\text{N}_2(g), \text{K}(s)]$ in which it exists at 1 atm and 25°C .

Heat of formation

- **The heat of formation Δh_{form}** is a Change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states.
- From the definition of enthalpy it follows that the enthalpy formation of simple substances (elements) is zero.
- The heats of substances usually amount to about 80-800 kJ/mole.

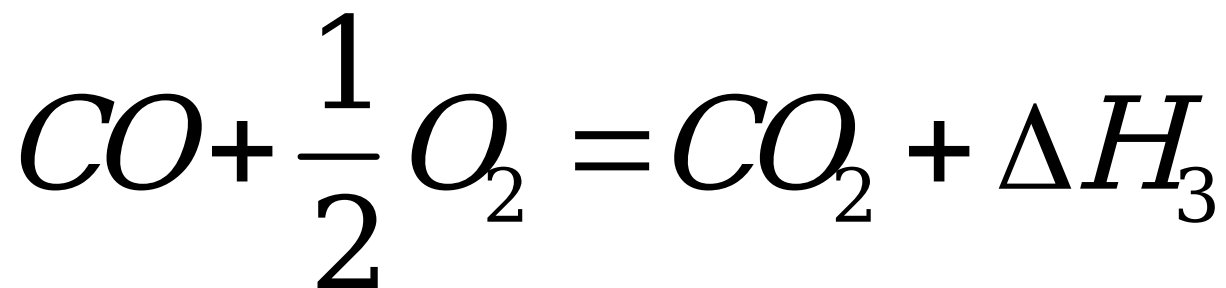
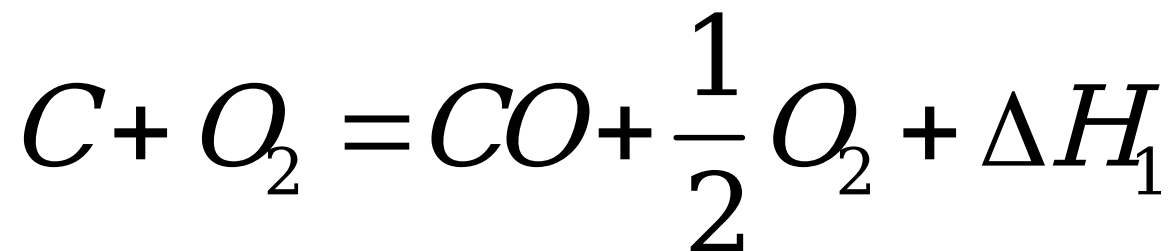


The heat of combustion

- **The heat of combustion** ΔH_{comb}
- the thermal effect of the chemical oxidation reaction of 1 mole of compound by oxygen with the formation of higher oxides or compounds of these oxides: CO₂ and H₂O
- The heat of combustion is exothermic, that is, energy is liberated through the combustion reaction.

The heat of combustion

- Typical combustion reactions involve the reaction of a carbon-containing material with oxygen to form carbon dioxide and water as products. If methanol is burned in air, we have:
- $\text{CH}_3\text{OH} + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ $\Delta H = -890 \text{ kJ/mol}$
- In this case, one mole of oxygen reacts with one mole of methanol to form one mole of carbon dioxide and two moles of water.
- It should be noted that inorganic substances can also undergo a form of combustion reaction:
- $2\text{Mg} + \text{O}_2 \rightarrow 2 \text{MgO}$
- In this case there is no water and no carbon dioxide formed. These reactions are generally not what we would be talking about when we



Heat of neutralization

- **Heat of neutralization** ΔH_{neutr} - the thermal effect of the interaction of 1 equivalent of acid and base.
- It consists of the heat of dissociation and proper neutralization. Experience shows that when sufficiently diluted water solutions of strong acids are neutralized by alkaline, regardless of nature, there is the same thermal effect:
- $\Delta H_{neutr} = 56 \text{ kJ/mole}$ If a weak acid or a weak base reacts, the heat of neutralization will be less, as the dissociation of acid (base) will require energy

Heat of neutralization

- The full equation for the reaction between hydrochloric acid and sodium hydroxide solution is:
- $\text{NaOH}_{\text{aq}} + \text{HCl}_{\text{aq}} = \text{NaCl}_{\text{aq}} + \text{H}_2\text{O}_{\text{l}}$
- . . . but what is actually happening is:
- $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
- If the reaction is the same in each case of a strong acid and a strong alkali, it isn't surprising that the enthalpy change is similar.
- The standard enthalpy change of neutralization is the enthalpy change when solutions of an acid and an alkali react together under standard conditions to produce 1 mole of water.

The heat of phase transitions

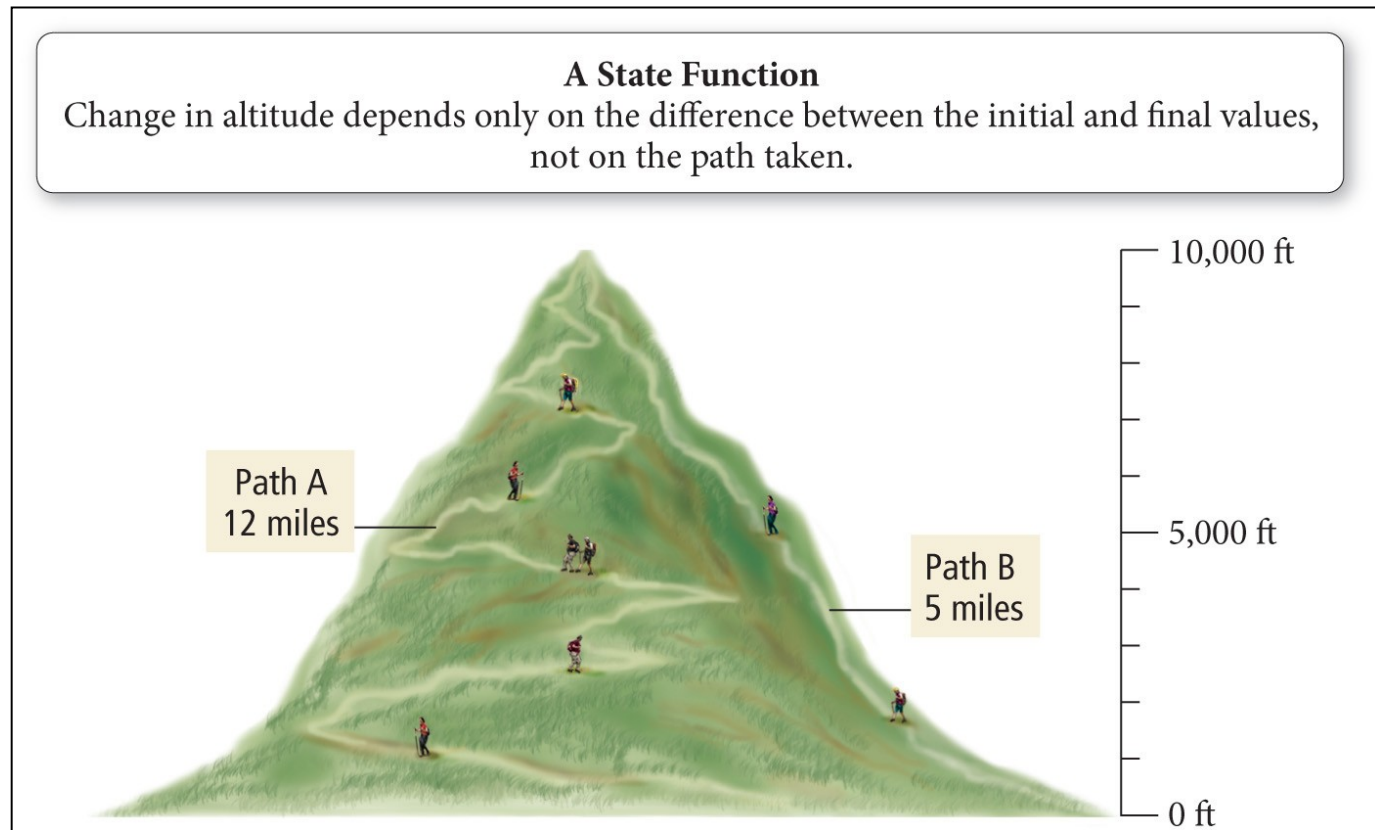
- **The heat of phase transitions $\Delta H^{\circ}_{f.t}$** - The thermal effect of the transition of 1 mole substance from one phase to another.
- The following form of recording of these values has been adopted: $\Delta_s H^{\circ}$, $\Delta_v H^{\circ}$, $\Delta_m H^{\circ}$. Letters s , v and τ are the first letters of the English words sublimation - "sublimation," vaporization - "evaporation" and melting - "melting."
- The heats of vapor formation have the values of order 40 kJ/mole, melting heat - about 4-20 kJ/mole;

The heat of dissolution

- Since the thermal effect of dissolution depends on the concentration of the solution, the thermochemical study of solutions uses several values describing the process.
- Integral heat of dissolution is called the change of enthalpy when 1 mole of matter is dissolved in a certain amount of solvent, which result in a solution with a given concentration.
- It is equal to the amount of absorbed heat when the crystal lattice is destroyed and the warmth of the ions are salted.
- Often this value is called simply the heat of dissolution.

What is a state function

- The change in altitude is a state function.
- The pathway is not

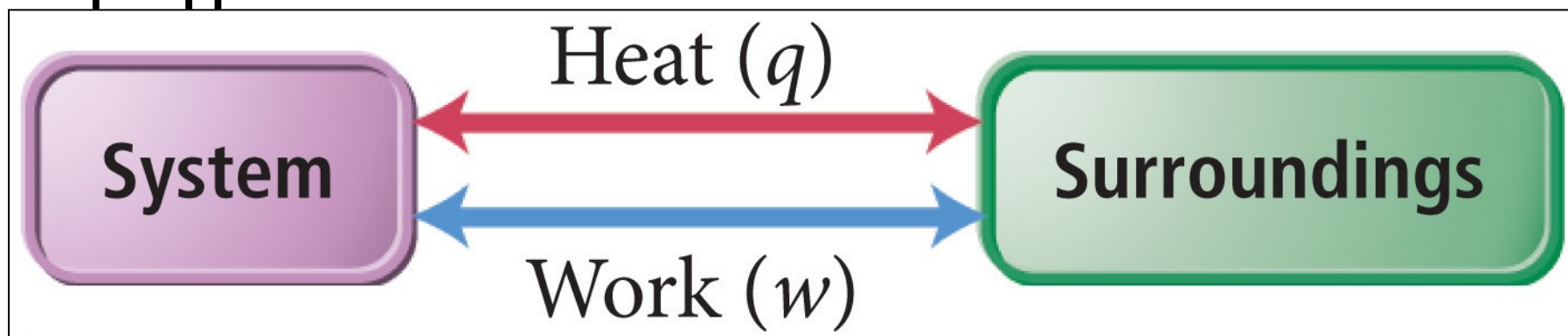


Change in Internal Energy

- Just like a change in altitude a change in internal energy is a state function.
- $\Delta U = U_{\text{final}} - U_{\text{initial}}$
- In a chemical system the reactants are the initial state (ground level) and the products are the final state (peak)
- $\Delta U = U_{\text{products}} - U_{\text{reactants}}$

Heat and Work: Pathways to Energy Change

- A system can exchange energy with its surroundings through heat, work, or heat.



- The change in Internal Energy is the sum of the heat exchanged and work done $\Delta U = q + w$

Heat and Work: Pathways to Energy Change

- $\Delta U = \text{heat} + \text{work} = q + w$
- When we looked at the change in altitude on the mountain we saw that the two pathways were very different.
 - The change in altitude was a state function (independent of path)
 - The pathways were not state functions
- Same situation for heat and work
- ΔU is a state function
 - q and w are not

Heat and Work: Pathways to Energy Change

- ΔU is a state function
 - q and w are not
- The amount of heat (or work) to attain a given change in internal energy depends on the pathway.
- Think about a gallon of gas
 - Burning in an open container (lots of heat, not much work)
 - Moving a car 40 miles (lots of work, less heat)
- Same change in internal energy but q and w are completely different depending on the path

1st Law of thermodynamic

- Internal energy U of a system is the sum of the kinetic and potential energies of all the “particles” in the system.
- To change the internal energy of a system:
$$\Delta U = q + w$$

q represents heat
 w represents work

ISOBARIC PROCESS

- In the isobaric process ($p = \text{const}$), the work of expansion A and for one mole of an ideal gas
$$A = - p(V_2 - V_1) = - p\Delta V$$
- Then
$$Q_p = \Delta U + p\Delta V = (U_2 - U_1) + p(V_2 - V_1) =$$
- $$= (U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1 = \Delta H,$$
- where $H = (U + pV)$ is called the enthalpy of the system. Enthalpy, like internal energy, is a function of the state, and its changes do not depend on the path of the process.

ISOCHORIC PROCESS

- In an isochoric process, the volume of the system does not change ($dV = 0$), therefore, the work of expansion is zero and
- $\delta Q_V = dU$, a $(dU/dT)_V = (\delta Q/dT)_V = c_V$
- where c_V is the specific heat at constant volume; for a monoatomic ideal gas it is equal to $3R/2$. It follows that
- $dU = c_V dT$ or $\Delta U = c_V \Delta T$
- Heat of the isochoric process
- $Q_V = U_2 - U_1 = \Delta U$.
- For an ideal gas equation is valid not only for isochoric, but for any process in which the volume and pressure vary arbitrarily.

Hess's law

In 1836, Herman Hess, a professor at the St. Petersburg Mining Institute, established the basic law of thermochemistry, which is essentially a consequence of the 1st law of thermodynamics.

Hess's law: the thermal effect of the physical and chemical process does not depend on the path of the process, but is determined only by the initial and final state of the system.

Conditions:

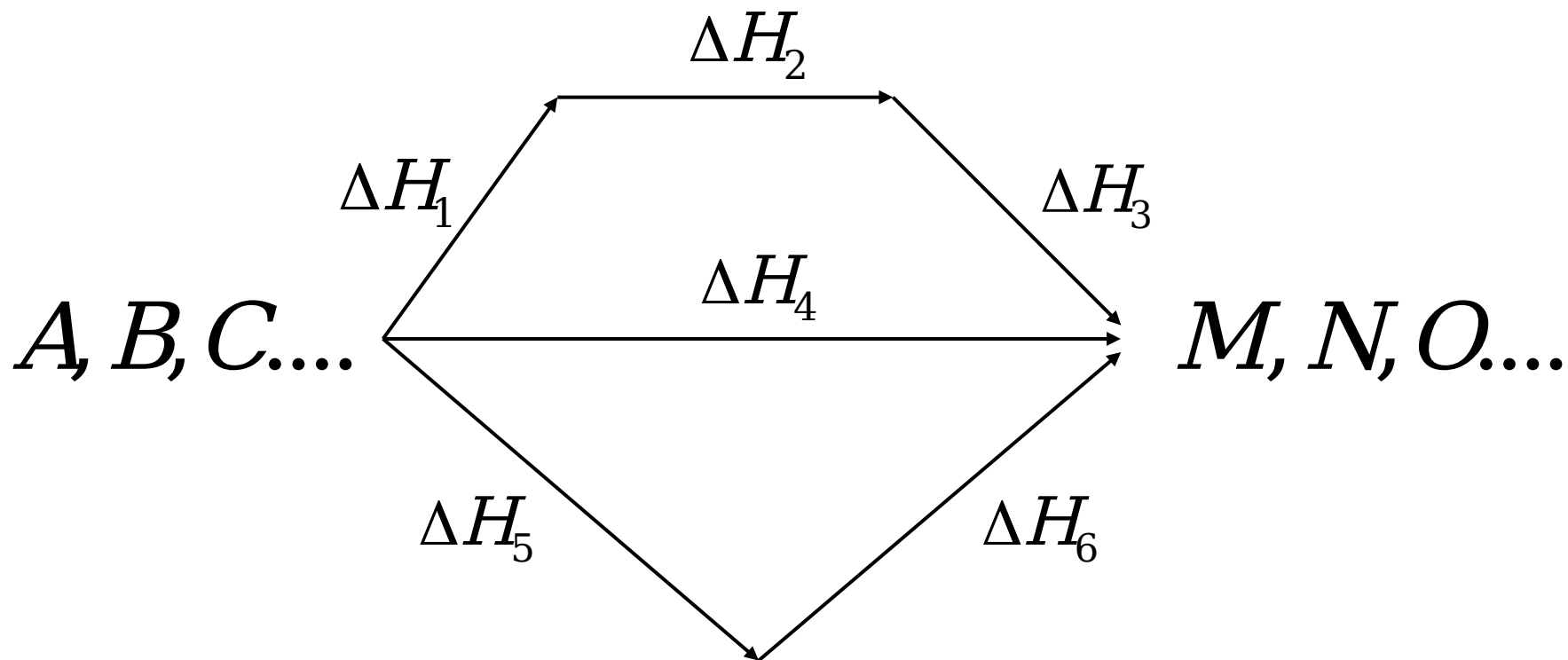
$P = \text{const}$ or $V = \text{const}$

$T = \text{const}$

Irreversible process

Heat on 1 mole substance

• **N.U.: $T 25^{\circ}\text{C}$ and $P 1 \text{ atm}$**



$$\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_5 + \Delta H_6$$

Consequence of Hess's Law

Hess's law allows for the treatment of thermochemical equations as algebraic, i.e. folding, subtracting, multiplying and dividing into whole and fractional numbers, if only the thermal effects are the same conditions.

For thermochemical calculations more often use the consequences of the law of Hess, which allow to determine the thermal effects of numerous physical and chemical processes, without resorting to measurements.

Consequence of Hess's Law

- **1st Consequence of Hess Law:** *the thermal effect of decomposition of a substance is exactly equal to the thermal effect of its formation (Lavoisier-Laplace's law)*



$$\Delta H_{\text{forward}} = - \Delta H_{\text{backward}}$$

Consequence of Hess's Law

2nd consequence : the thermal effect of the reaction is equal to the algebraic amount of the heat of formation reaction products minus the algebraic amount of the heat of the formation of the initial substances taking into account the stoichiometric coefficients.

Consequence of Hess's Law



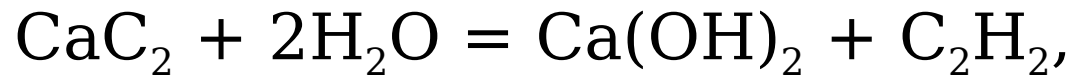
$$\Delta H_{reaction} = \sum \Delta H_{form prod.} - \sum \Delta H_{form init.}$$

$$\Delta H_P = (2\Delta H_{form}^{CO_2} + 3\Delta H_{form}^{H_2O}) - (\Delta H_{form}^{C_2H_5OH} + 3\Delta H_{form}^{O_2})$$

$$\Delta H_{form}^{O_2} = 0$$

$$\Delta H_P = (2\Delta H_{form}^{CO_2} + 3\Delta H_{form}^{H_2O}) - (\Delta H_{form}^{C_2H_5OH})$$

Determine the thermal effect of the reaction



If the heats of formation of CaC_2 , H_2O , Ca(OH)_2 and C_2H_2 are equal to 62760; - 285838; -986587 and 226731 J/mole respectively.

- **Solution.** The sum of the heats of formation of the reaction products is equal to

- $-986587 + 226731 = -759856 \text{ J.}$

- The sum of the heats of formation of the starting materials is equal to

- $-62760 + 2 (-285838) = -634436 \text{ J.}$

- The sought heat is equal to

- $-759856 - (-634436) = -125420 \text{ J.}$

Consequence of Hess's Law

3rd Consequence : the thermal effect of the reaction is equal to the algebraic amount of enthalpy of combustion of the initial substances minus the algebraic amount of enthalpy of combustion products taking into account their stoichiometric coefficients.

Consequence of Hess's Law



$$\Delta H_{reaction} = \sum \Delta H_{comb.init.} - \sum \Delta H_{comb.prod.}$$

$$\Delta H_P = (\Delta H_{comb}^{C_2H_5OH} + 3\Delta H_{comb}^{O_2}) - (2\Delta H_{comb}^{CO_2} + 3\Delta H_{comb}^{H_2O})$$

$$\Delta H_{comb}^{O_2} = 0 \quad = 0$$

$$\Delta H_{comb}^{H_2O} = 0$$

$$\Delta H_P = \Delta H_{comb}^{C_2H_5OH}$$

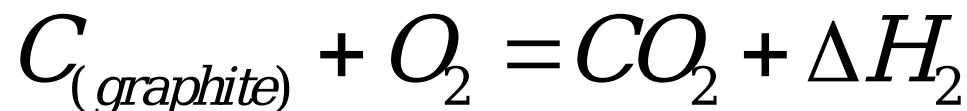
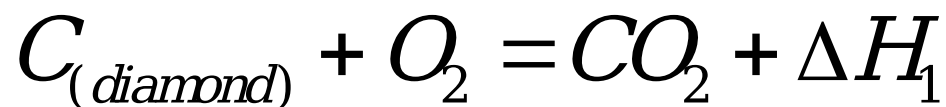
Calculate the heat of hydrolysis of maltose at constant pressure: $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$ if there are heat combustion of maltose and glucose ΔH° of combustion (maltose) = -5610 kJ / mol, ΔH° of combustion (glucose) = -2801.69 kJ / mol.

- $\Delta H = (\Delta H_{c.m.} + \Delta H_{c.w.}) - 2 * \Delta H_{c.g.} =$
- $= \Delta H_{c.m.} - 2 * \Delta H_{c.g.} =$
- $= -5610 - 2 * (-2801.69) = -5610$
 $+ 2 * 2801.69 =$
- $= -5610 + 5603.38 = -6.62 \text{ kJ}$

Consequence of Hess's Law

4th Consequence: *if there are two reactions that lead from different initial states to the same end states, the difference between their thermal effects is the thermal effect of moving from one initial state to another. This effect allows you to accurately calculate the thermal effects of processes that are often not even possible to practically implement.*

Consequence of Hess's Law

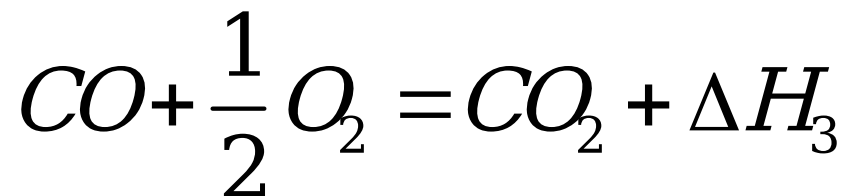
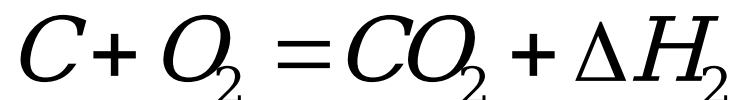
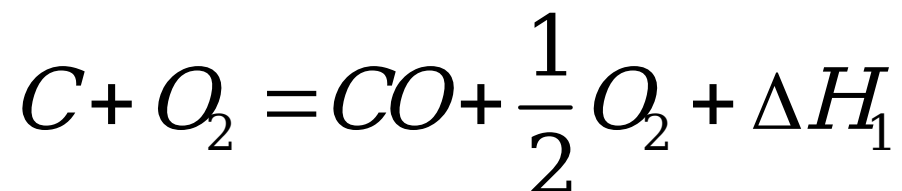


$$\Delta H_3 = \Delta H_1 - \Delta H_2$$

Consequence of Hess's Law

5th Consequence: *if there are two reactions that lead from the same initial states to different end states, the difference between their thermal effects is the process of transition from one end state to another.*

Consequence of Hess's Law



$$\Delta H_3 = \Delta H_2 - \Delta H_1$$